

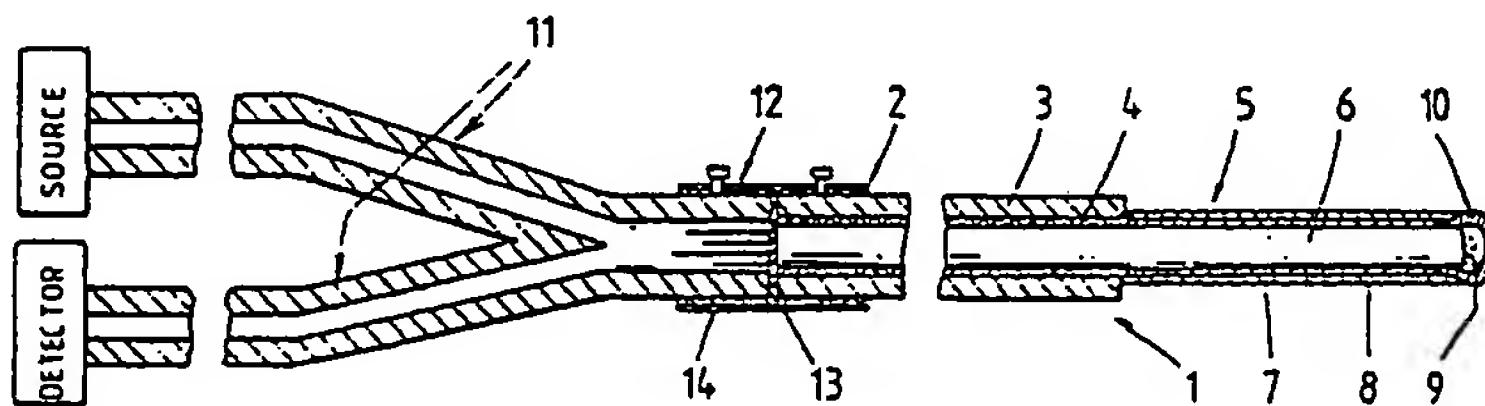


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(54) Title: FIBRE OPTIC CHEMICAL SENSOR



(57) Abstract

A sensor (1) for detecting changes in or monitoring the level of a chemical parameter of interest, comprising an optical fibre cable (2) having a sensing segment (5) that is a film coating of a support matrix (7) on the core (6) of the optical fibre cable with any sheathing and cladding removed, on which support matrix is immobilized an indicator compound having spectral characteristics sensitive to the parameter of interest, wherein the support matrix consists of a material permeable to the species of interest. Embodiments wherein the sensor is configured as a probe are also disclosed.

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FIBRE OPTIC CHEMICAL SENSOR

5 This invention relates to fibre optic chemical sensors.

There have been two major trends in the development of these sensors. One is to immobilize a chemical indicator in a matrix, at the end of a fibre optic light guide, and to 10 observe and process the signal reflected from the matrix. A second approach is to bind a suitable matrix containing the immobilized indicator on to the surface of a fibre optic light guide, and to observe and process the transmitted signal. In some cases this signal may be purposefully reflected back 15 along the same fibre optic light guide for observation. It is

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also possible to bind the indicator to the fibre optic light guide surface, either directly, or by using an intermediary binding agent.

A certain amount of success has been achieved using
5 both of these approaches e.g. in U.S. patent application No. 855,397 (Peterson, 1980), in I.C.I. PLC's European patent applications No. 82301495.6, No. 82301496.4, and No. 82303803.9, and in British patent applications No. 8313527 and No. 8314519 by Elf U.K. PLC.

10 In all of these applications the fibre optic probe was used in conjunction with a porous material.

Description of the Invention

This invention relates to a sensor for monitoring a change in, or measuring the level of, a chemical parameter of
15 interest, e.g. a chemical parameter such as the nature or concentration of a chemical species in solution or in the gaseous phase.

Various types of electrical sensors are already known. These sensors do however have a number of
20 disadvantages. Firstly, the sensors rely on the use of electrical signals, which may be undesirable if the sensor is to be used in an inflammable environment. Secondly, there may be impedance effects in the electrical sensor which adversely affect the measurement being made. The problems associated
25 with impedance effects become particularly acute when miniaturized sensors are required. In such a case, it may be necessary to operate the sensor within a Faraday cage to avoid the impedance effects.

— It is an object of this invention to provide a
30 sensor which obviates or mitigates the above disadvantages, and which also overcomes the problems of increased reflectance and scatter of light, and of insufficiency in the amount of light collected, which have been experienced using fibre optic sensors with a porous coating. It is a further object of the

invention to provide a fibre optic sensor which resists leaching of the indicator material from the surface of the sensor.

According to the present invention there is provided a sensor for detecting changes in or monitoring the level of a chemical parameter of interest, which sensor comprises an optical fibre cable having a sensing segment that is a film coating of a material (henceforth known as the support matrix) on the core of the optical fibre cable with any sheathing and cladding removed, and on this said material is immobilized a compound (henceforth known as the indicator compound) having spectral characteristics sensitive to the parameter of interest. The support matrix consists of a material permeable to the species of interest. Further, when configured as a probe a tip is incorporated, this tip being either reflective, absorptive or a combination of both. Also a second outer film coating of a different material to the support matrix may be incorporated.

The sensor of the invention is suitable for use in an aqueous environment, in non-aqueous liquid environments, and in gaseous environments. For long-term use in the latter two cases, a constant minimum water content of the environment is preferred.

The optical fibre cable provides the means for transmitting light to the indicator compound from a light source, and for transmitting light from the said indicator compound to a detector. The detector may be set to detect a change or level in a property of the light affected by the indicator compound; e.g. a property such as the intensity or wavelength of the light. A single fibre means is preferred to form the core of the sensing segment, although a multiple fibre bundle may be employed to conduct light to the single fibre from the source and from the single fibre to the detector. This method simplifies the support instrumentation required when the sensor is configured as a probe. Multiple

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fibre bundles with a bundle size comparable with the single fibre means, are physically abutted to the single fibre in a snugly fitting tube arrangement. Gel or fluid of refractive index matching that of the fibre may be employed at the joint 5 to reduce undesirable reflections and losses.

The support matrix is a polymer material chosen to have an index of refraction similar to that of the core material of the optical fibre cable. In this way the light interaction with the immobilized indicator compounds is 10 maximized, and only short lengths of sensing segment are required. A second and important function of the support matrix is to act as a permeable membrane which allows or excludes certain parameters from interaction with the indicator compound, e.g. a hydrophobic support matrix such as 15 poly (methyl methacrylate) will exclude at its surface ionized species, thus hydrogen (hydronium) ions are not able to affect a colorimetric pH indicator when this is the immobilized indicator compound.

Another material (henceforth known as the sensor 20 cladding material, which may be different from the original cladding material used on the optical fibre means) may be used to provide both optical and chemical isolation of the sensor segment from the environment under investigation. Optical isolation is best achieved when the index of refraction of the 25 sensor cladding material is similar to that of the cladding material used on the optical fibre means.

The cladding material may also be based on the same material as the support matrix, but fabricated in such a way as to produce a gradient refractive index change radially from 30 the core material.

The degree of optical isolation obtained is similar whether the sensor cladding material is incorporated as a step refractive index change or a gradient refractive index change.

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It is possible to have multiple film coatings, using films with different properties, although such multiple coatings will result in a slower response. The use of a sensor cladding material as described is not always preferred.

5 All the coating layers are desirably as thin as is practicable, in order to attain the most rapid access by diffusion of the species of interest to the indicator material and hence to attain the most rapid response time possible.

The indicator compound is at least one reagent which 10 undergoes a change in its spectral characteristics in response to a change in the parameter of interest, e.g. a change in the nature or concentration of a particular chemical species. The spectroscopic change may be one of luminescence or absorption. Suitable indicator compounds are the colorimetric and 15 fluorimetric indicator dyestuffs, chosen with regard to the parameter of interest, e.g. bromothymol blue or bromocresol purple may be used to determine ammonia concentration. The indicator may be physically contained within the sensor support matrix or held by non-covalent interactions.

20 When configured as a probe it is important to define accurately the boundary conditions at the tip of the sensor. The primary purpose of this is to ensure that the light reflection at that extremity is constant and independent of the environment under investigation. An absorptive tip 25 ensures that light escaping at the end of the probe does not reflect back into the probe regardless of the environment under investigation. A reflective tip enables a substantial proportion of the light that would normally escape the probe to be reflected back into the probe. This may be 30 advantageous, especially when the indicator compound used in the sensor is of the absorptive type. It is preferred in practice to use an absorptive, or an absorptive and reflective tip, e.g. a metal-loaded material or a two-layer combination, to reduce environmental effects.

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The invention will be further described by way of examples incorporating the features so far outlined, and with reference to the accompanying drawings in which:

Figure 1 represents a sectional view of the sensor 5 in one embodiment of the probe in accordance with the invention;

Figure 2 represents the response time of the probe to NH₄OH;

Figure 3 represents a sectional view of an 10 alternative embodiment of the probe in accordance with the invention; and

Figure 4 represents a sectional view of an embodiment in which the sensor of the invention is configured in line with the detector.

15 The probe (1) shown in Figure 1 comprises an optical fibre cable (2) (including sheathing (3) and original cladding (4)) and a sensing segment (5) at one extremity of the optical fibre cable (2). The sensing segment itself comprises the core (6) of the optical fibre cable (2) with a film coating of 20 the support matrix (7) containing the immobilized indicator compound, and an outer film coating of a cladding material (8), and with a combination reflective (9) and absorptive (10) tip.

In use, the probe of the invention is associated 25 with a light source and a light detector. Light from the source is transmitted along the multiple fibre bundle (11) to the optical fibre cable (2) and on to the indicator compound, through the abutted joint (12). Reflections and losses at the joint are reduced by index-matching gel or fluid (13). The 30 two types of cable are held concentric and in close proximity by a snugly fitting and clamped tube (14), providing a quickly and easily separable joint. Light from the indicator compound is transmitted along the optical fibre cable (2), and a

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proportion of the light is collected by about half of the multiple fibre bundle (11) at the abutted joint (12) and transmitted on to the detector.

To give an idea of the size, the sensing segment (5) 5 of the probe (1) may be of length about 10 mm whereas the optical fibre cable (2) may have a core (6) diameter of 1 mm. These dimensions are given purely by way of an example and may of course be different to suit particular applications for the probe (1). In particular, miniaturization or encasement in a 10 hypodermic needle would allow use of the probe in clinical and other biomedical applications.

Example 1

The sensor configured as a probe as shown in Figure 1 may be used to determine the concentration of ammonia in 15 aqueous solution. In this application it is preferred that a sensing segment cladding (8) is not employed unless immiscible oils and solvents are likely to be present in the aqueous solution. As has already been mentioned, an indicator compound such as bromothymol blue or bromocresol purple may be 20 used, immobilized in a support matrix (7) of poly (methyl methacrylate) which is coated on an optical fibre core (6) which may be of the same material. A combination or metallised tip (9) and (10) as illustrated is preferred in this particular application. Light of wavelength in the 25 mid-visible region (about 590 nm) is strongly absorbed by the two indicator compounds mentioned, in their base form. In the presence of ammonia these indicator compounds exist in two conjugate forms, the acid form and the base form. The higher the concentration of ammonia present, the greater the 30 proportion of the base form of the indicator compound in the conjugate combination. If the source used to provide light to interact with the indicator compound emits in the wavelength region about 590 nm, then the proportion that is absorbed by the indicator compound may be related to the concentration of 35 ammonia. The detector is used to detect the level of light

absorbed with reference to another wavelength region. In this particular example, the reflective nature of the tip greatly enhances the light received at the detector and therefore assists in the determination of the proportion of light 5 absorbed.

The probe may thus be used simply to indicate a change in ammonia concentration. Alternatively the probe may previously have been calibrated so that the level of, or change in intensity of the partially absorbed light gives a 10 quantitative indication of the concentration of, or change in concentration of ammonia.

The polymer materials used are permeable to ammonia, methylamine, and ethylamine, although the response time with ethylamine is somewhat prolonged. It appears that the size 15 limit of molecules able to penetrate the polymer is of the order of 3Å.

The sensor function is relatively insensitive to the temperature and ionic strength of the environment, and can operate in the short term in a water-free environment.

20 The response to NH_4OH of a probe using bromothymol blue as indicator with the wavelength of light provided by the source using 1 L water to which different volumes of 30% NH_3 solution had been added, has its maximum at approximately 584 nm.

25 To determine the response time of the probe, NH_3 (as a 30% solution in water) was added to a reservoir of 1.0 L of distilled water at 24°C. The results are shown in Fig. 2, which represents a chart recording of the response of a bromothymol blue coated probe with reflective tip monitored at 30 580 nm.

Example 2

The sensor configured as a probe as shown in Figure 1 may be used to determine the pH of a solution. In this application, the sensing segment cladding (8) is not required

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to achieve optical isolation. Fabrication methods may be employed that enable a gradient index to form from the fibre core (6) to the support matrix (7) outer surface. This gradient index appears when the probe is in an aqueous 5 operational environment and the support matrix (7) has become hydrated. The support matrix (7) is designed to have a diffusion profile into the surface of the core material (6), so that when this matrix becomes hydrated it will cause a gradient in the radial index, rather than an abrupt or step 10 change. Because of this gradient index, total internal reflection within the probe will occur before the outermost surface boundary, thus providing optical isolation.

The preferred materials used as the support matrix (7) are the hydroxylated acrylates and methacrylates. To 15 ensure permanent immobilisation of the indicator on the support matrix (7) under conditions where the matrix swells considerably and extreme values of pH can occur, it is also preferred to covalently bond the indicator. With the preferred hydroxylated matrixes, reactive indicators have been 20 used, some of which are commercially available, i.e. Procion Brilliant Red. However there are numerous other bonding techniques recorded in the literature.

Example 3 Alternative Configuration as a Probe

In another preferred embodiment of the invention, 25 shown in Figure 3, the probe (1) comprises an optical fibre cable (2) (including the core (3) and cladding (4) and optionally including sheathing (5)), and a sensing segment (6) at one extremity of the optical fibre cable (2). The sensing segment (6) itself comprises a thin coating of the support 30 matrix (7) permanently bound on the exposed face of the fibre cable (2) at the distal end. The support matrix (7) contains an immobilised indicator compound.

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In use, the probe of the invention is associated with a light source and a light detector. Light from the source is transmitted along the optical fibre cable (2) and is incident upon the support matrix (7). Although some of the 5 light maybe reflected at the boundary with the support matrix (7), that which is not reflected will be transmitted through the support matrix (7) and will interact with the immobilised indicator. Some of the backscattered or re-emitted light from the immobilised indicator is collected by the optical fibre 10 and transmitted on to the detector.

It is not important that the coating covers the sheathing and cladding, but it is important that it covers the core material completely, and that the cladding covers the core and is adjacent to the coating.

15 The 'distal end' of the optical fibre is the end furthest from a connection point to the associated instrumentation. In contrast, the 'proximal end' is the end of the optical fibre attached to the instrumentation. For a 'probe' of this second configuration, it is a necessary 20 condition that the coating is at the distal end of the transmitting fibre, although a second optical fibre might be employed to pick up the transmitted optical signal and conduct it back to the detector. In a 'sensor' of the original configuration, the sensing segment does not necessarily have 25 to appear at any end of the optical fibre and may be any distance along it. However when termed a 'probe' it is implied that the sensing segment is at the distal end of the fibre.

A 'probe' of this second configuration may have a 30 support matrix of either a translucent or transparent nature depending on the immobilised indicator compound employed. An absorptive indicator would be best bound in a scattering translucent matrix, whereas a fluorescent indicator would prove more effective in a transparent matrix.

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Example 4 Inline Sensor Configuration

As illustrated in Figure 4, the sensor (1) comprises an optical fibre cable (2) (including the core (3) and cladding (4) and optionally including sheathing (5)), and a sensing segment (6) at any point along the length of the optical fibre (2). The sensing segment (6) itself comprises a film coating of the support matrix (7) on the core (3) of the optical fibre cable (2) with the cladding (4) and sheathing (5) removed. The support matrix (7) contains an immobilised indicator compound. A further film coating (8) may be applied over the support material to act as cladding or as a membrane permeable to a specific chemical species.

In use, the probe of the invention is associated with a light source and a light detector. Light from the source is transmitted along the optical fibre cable (2) to the sensing segment where it will interact with the indicator compound immobilised on the support matrix (7). An indicator modified light signal is then transmitted further along the optical fibre cable (2) to the detector.

20 Advantages

1. The indicator material of the present invention is permanently bound within the permeable polymer coating.
2. The indicator is not subject to losses by leaching into the medium.
3. The polymer coating does not scatter light and so does not diffuse the signal.
4. The sensor of the present invention can be used in a variety of different environments.
- 30 5. The probe according to the invention is robust, with a long lifetime.
6. The probe can be miniaturized, or configured in a hypodermic needle or a catheter for biomedical or clinical use.

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Possible applications include:

1. Measurement of ammonia levels (using for example bromothymol blue or bromocresol purple as indicator).
- 5 2. Measurement of oxidation/reduction reactions.
3. Measurement of pH.
4. Measurement of fluorescence or other luminescence.
5. Remote sensing of a variety of parameters.
6. Measurement of a variety of parameters in vivo in
10 humans or animals.
7. Measurement of metal ion levels using metallocromic indicators.
8. Measurement of organic functional groups using appropriate indicators.

15 It will be clearly understood that the invention in its general aspects is not limited to the specific details referred to hereinabove.

CLAIMS

1. A sensor for detecting changes in or monitoring the level of a chemical parameter of interest, which comprises an optical fibre cable having a sensing segment that is a film coating of a support matrix on the core of the optical fibre cable with any sheathing and cladding removed, on which support matrix is immobilized an indicator compound having spectral characteristics sensitive to the parameter of interest, wherein the support matrix consists of a material permeable to the species of interest.
2. A sensor according to Claim 1 further incorporating a second outer film coating of a material different to that of the support matrix.
3. A sensor according to Claim 1 or Claim 2 wherein the optical fibre cable comprises a single fibre means.
4. A sensor according to Claim 1 or Claim 2 wherein a multiple fibre bundle is employed to conduct light to the single fibre from the source and from the single fibre to the detector.
5. A sensor according to Claim 4 wherein multiple fibre bundles with a bundle size comparable with the single fibre means, are physically abutted to the single fibre in a snugly fitting tube arrangement, and gel or fluid of refractive index matching that of the fibre is contained in the tube surrounding the joint.
6. A sensor according to any preceding claim wherein the support matrix is a polymer material chosen to have an index of refraction similar to that of the core material of the optical fibre cable.
7. A sensor according to Claim 6 wherein the support matrix is hydrophobic.
8. A sensor according to Claim 6 wherein the support matrix is poly(methyl methacrylate).
9. A sensor according to Claim 6 wherein the support matrix is a hydroxylated acrylate.

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10. A sensor according to Claim 6 wherein the support matrix is a hydroxylated methacrylate.
11. A sensor according to any previous claim wherein a sensor cladding material, which may be different from the original cladding material used on the optical fibre means is used to provide both optical and chemical isolation of the sensor segment from the environment under investigation.
12. A sensor according to Claim 11 wherein the refractive index of the sensor cladding material is similar to that of the cladding material used on the optical fibre means.
13. A sensor according to Claim 11 wherein the cladding material is based on the same material as the support matrix, but fabricated in such a way as to produce a gradient refractive index change radially from the core material.
14. A sensor according to any one of Claims 11 to 12 wherein the sensor cladding material produces a step refractive index change radially from the core material.
15. A sensor according to any previous claim wherein multiple film coatings are used, characterized in that the films have different properties.
16. A sensor according to any previous claim wherein the indicator compound is at least one reagent which undergoes a change in its spectral characteristics in response to a change in the parameter of interest.
17. A sensor according to Claim 16 wherein the spectral change is one of luminescence.
18. A sensor according to Claim 16 wherein the spectral change is one of absorption.
19. A sensor according to Claim 16 wherein the indicator compound is held within the sensor support matrix by covalent bonding.
20. A sensor according to Claim 16 wherein the indicator compound is physically contained within the sensor support matrix.

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21. A sensor according to Claim 16 wherein the indicator compound is held within the sensor support matrix by non-covalent interactions.
22. A sensor according to any one of Claims 16 to 21 wherein the indicator is sensitive to pH, redox potential or ammonia.
23. A probe characterized in that a tip is incorporated into a sensor according to any previous claim.
24. A probe according to Claim 23 wherein the tip is reflective and/or absorptive.
25. A probe according to Claim 23 further characterized in that it is incorporated into a hypodermic needle, endoscope or catheter.
26. A probe according to Claim 23 comprising an optical fibre cable, including sheathing and original cladding and a sensing segment at one extremity of the optical fibre cable; wherein the sensing segment itself comprises the core of the optical fibre cable with a film coating of the support matrix containing the immobilized indicator compound, and an outer film coating of a cladding material, and with a combination reflective and absorptive tip.
27. A probe according to Claim 23 comprising an optical fibre cable including the core and cladding and optionally including sheathing, and a sensing segment at one extremity of the optical fibre cable, wherein the sensing segment itself comprises a thin coating of the support matrix permanently bound on the exposed face of the fibre cable at the distal end, and the support matrix contains an immobilised indicator compound.
28. An inline sensor comprising an optical fibre cable including the core and cladding and optionally including sheathing, and a sensing segment at any point along the length of the optical fibre, wherein the sensing segment itself comprises a film coating of the support matrix on the core of

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the optical fibre cable with the cladding and sheathing removed, and the support matrix contains an immobilised indicator compound.

29. An inline sensor according to Claim 28 wherein a further film coating is applied over the support material to act as cladding or as a membrane permeable to a specific chemical species.

30. Apparatus for detecting changes in a chemical parameter which incorporates a sensor or probe according to any previous claim.

31. A method for estimation of ammonia, methylamine or ethylamine characterized by the use of a sensor or probe according to the invention.

32. A method for determination of pH characterized by the use of a sensor or probe according to the invention.

33. A method for determination of redox potential characterized by the use of a sensor or probe according to the invention.

34. Products and processes as hereinbefore defined with reference to the examples and drawings.

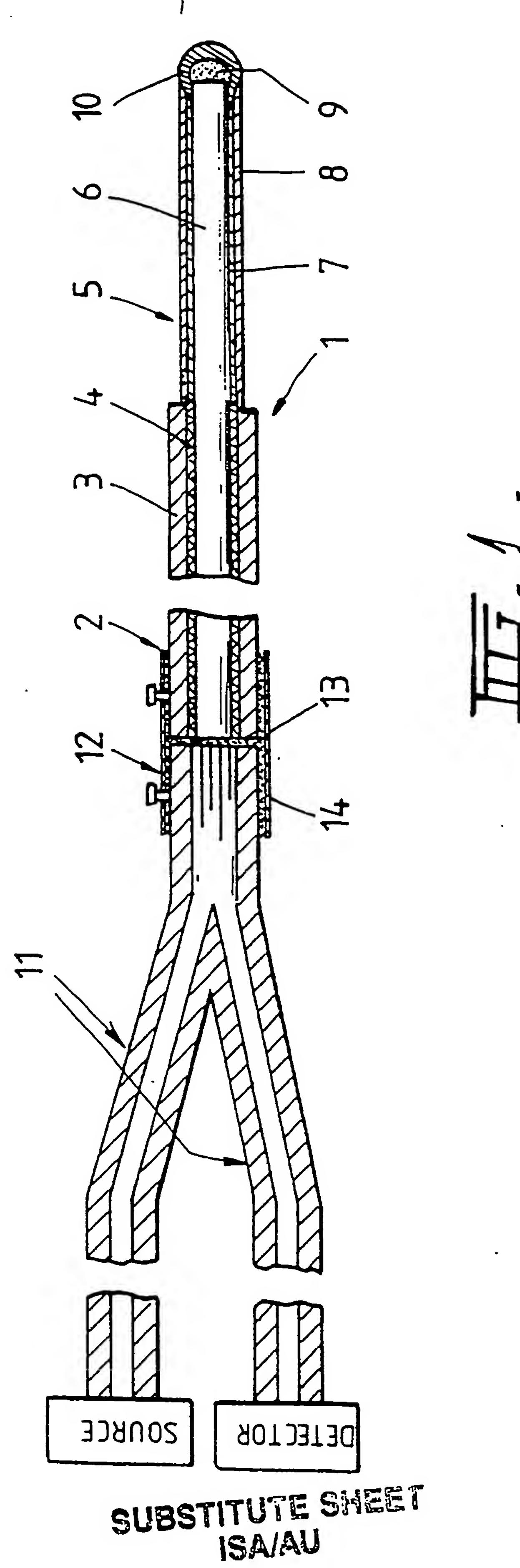
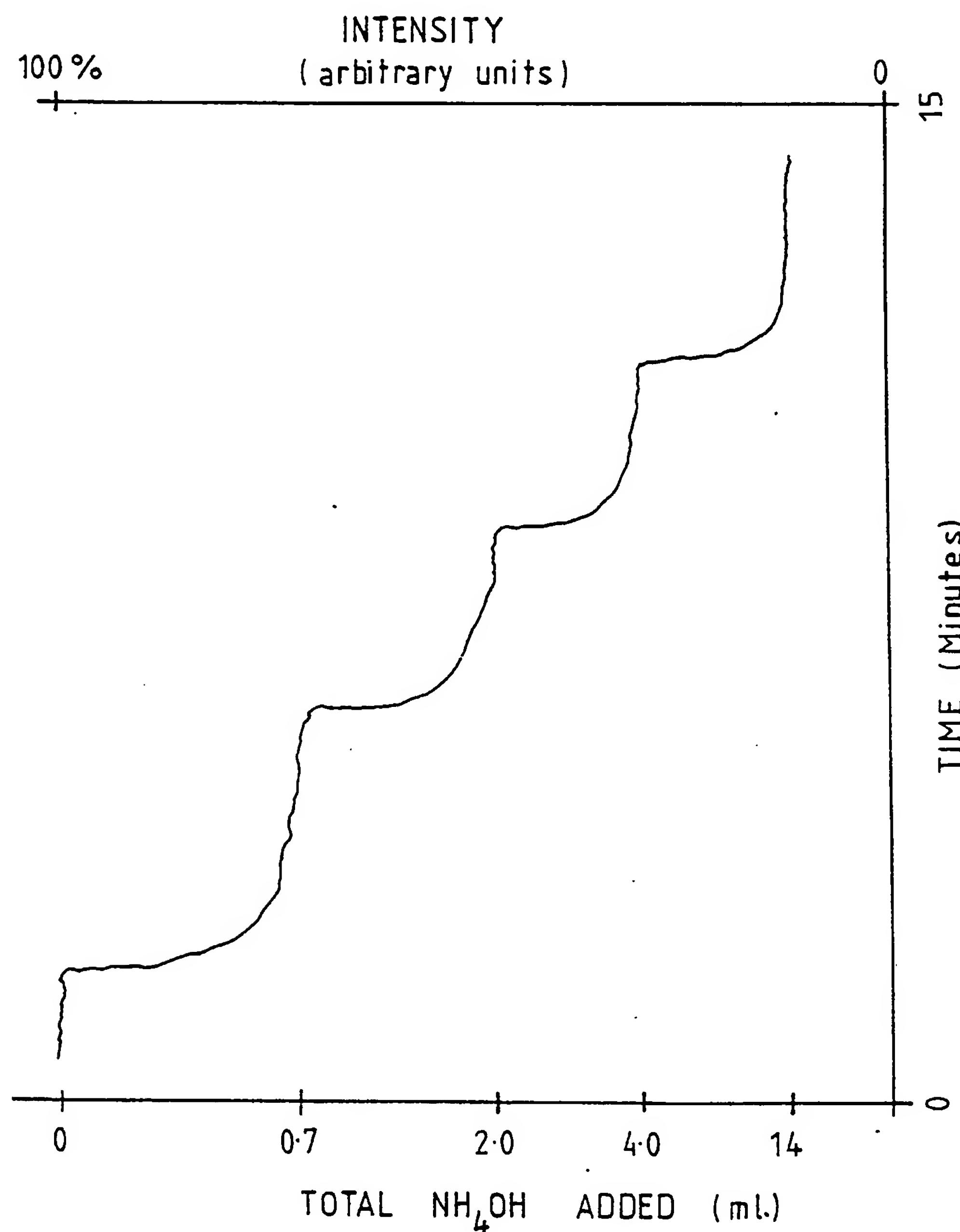
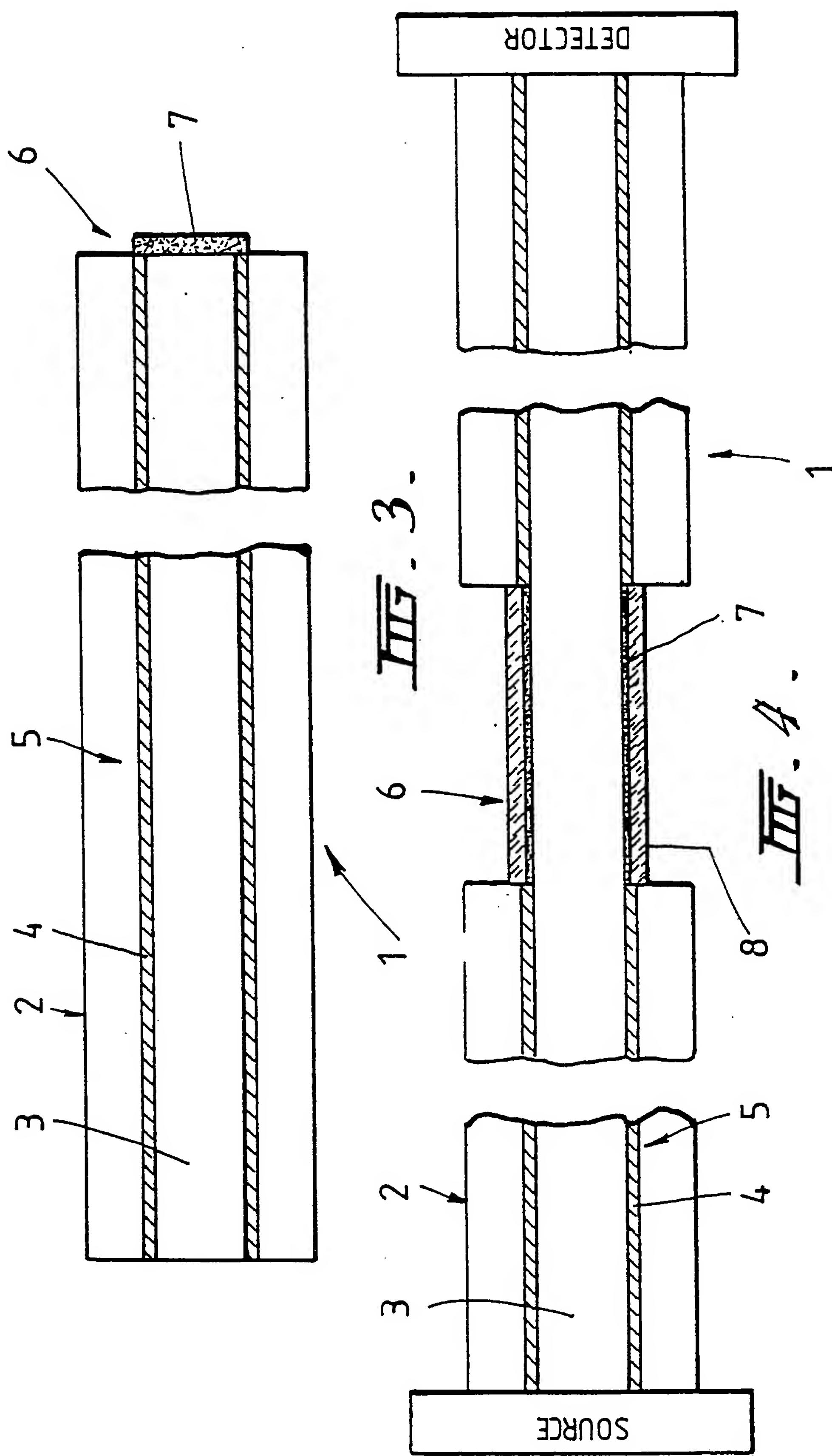


FIG. 2.

Bromothymol Blue/coated probe
with reflective tip monitored
at 580nm.





INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 86/00062

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl⁴ G01N 21/78

II. FIELDS SEARCHED

Minimum Documentation Searched¹

Classification System	Classification Symbols
IPC G01N 21/06, 21/08, 21/10, 21/77, 21/78, 21/79, 21/80, 21/81	

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched²

AU: IPC as above, G01N 31/22

III. DOCUMENTS CONSIDERED TO BE RELEVANT³

Category ⁴	Citation of Document, ⁵ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
-----------------------	---	-------------------------------------

- X EP, A, 126600 (ELF U.K. PLC)
28 November 1984 (28.11.84)
- X,Y EP, A, 72627 (Imperial Chemical Industries PLC)
23 February 1983 (23.02.83)
- X, Y EP, A, 61884 (Imperial Chemical Industries PLC)
6 October 1982 (06.10.82)
- Y EP, A, 73558 (The United States of America)
9 March 1983 (09.03.83)
- Y US, A, 4200110 (Peterson et al) 29 April 1980
(29.04.80)
- Y WO, A, 83/03344 (The United States of America)
13 October 1983 (13.10.83)
- Y ANALYTICAL CHEMISTRY, Volume 52, 1980, pages
864-869 (American Chemical Society, Washington
D.C., USA)
J.I. Peterson et al "Fiber Optic pH probe for
physiological use" See pages 865-866

* Special categories of cited documents:¹⁰
 "A" document defining the general state of the art which is not
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IV. CERTIFICATION

Date of the Actual Completion of the International Search

20 May 1986 (20.05.86)

Date of Mailing of this International Search Report

(27-05-86) 27 MAY 1986

International Searching Authority

Australian Patent Office

Signature of Authorized Officer

D. Herald

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

P, Y | US, A, 4557900 (Heitzmann)
10 December 1985 (10.12.85)

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This International search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claim numbers....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this International application as follows:

1. As all required additional search fees were timely paid by the applicant, this International search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this International search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this International search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

The additional search fees were accompanied by applicant's protest.
 No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 86/00062

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members		
EP	126600	GB	8313527	JP 60035246
EP	72627	GB	2103786	JP 58077641
EP	61884	JP	57174798	
EP	73558	JP	58038540	
US	4200110	CA	1121242	DE 2851138
		GB	2009394	JP 54085588
WO	8303344	AU	90592/82	CA 1187386
		US	4476870	EP 91390

END OF ANNEX

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